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INTERNAL TEMPERATURES AND GASSING CHARACTERISTICS OF A NiCd CELL FOR 37 PERCENT DEPTH OF DISCHARGE 90-MINUTE CYCLING

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ABSTRACT

An experimental 12-ampere-hour, nickel-cadmium electrochemical cell with eight internally mounted thermocouples was constructed and cycled on a 90-minute orbit. For a 37 percent D.O.D. orbit and 1.49-volt circuit, the internal temperature varied from 1.75C° above ambient (room temperature) at the end of discharge to 1.25C° below ambient after 30 minutes of charging. The temperature gradient for the plate stack averaged about 1C°, with the geometric center being the warmest position and the lower plate stack corners being the coolest. The reverse charging (5 amperes) of the cell yielded two voltage plateaus. The first plateau occurred at -0.1 to -0.3 volts, with the cell gassing hydrogen. Stopping the reverse charging at this point allows the cell to recover to a positive (normal, although less than 1 volt) voltage. However, if the reverse charging current is stopped at the second plateau (occurring at -1.56 volts with hydrogen and oxygen being liberated), the cell voltage would remain negative for several days.

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CONTENTS

	<u>Page</u>
Abstract	iii
INTRODUCTION	1
THE NiCd CELL	1
PROCEDURE	3
RESULTS	5

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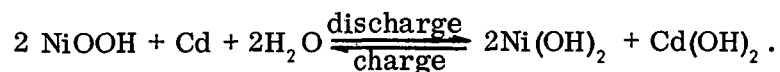
Goddard Space Flight Center

INTRODUCTION

Many spacecraft such as OAO and OGO use temperature parameters (thermal switches) to limit battery overcharging or thermal runaway. The electrical characteristics of spacecraft cells are also temperature-dependent. The heating characteristics of these cells must be known for heat sink requirements, thermal environment, and spacecraft energy balance. High temperature has been shown to adversely affect cell life by accelerating both the degradation of the separator and the deterioration of the cadmium electrode. Temperature and heating parameters are also needed to investigate the basic chemical processes of which much remains unexplained. The purpose of this work was to determine these internal temperature changes of a cell during cycling.

THE NiCd CELL

The main reaction occurring in a nickel-cadmium cell is thought to be



The heat of reaction for this change is 33 kilocalories per gram equivalent weight. Within any cycle, a spacecraft cell will have an endothermic and a exothermic period. During the charging period of a cycle, the cell will absorb heat (endothermic), and during the discharge it will liberate heat (exothermic). The situation is complicated further by heat from I^2R and numerous side reactions. The heat energy generated

(or absorbed) cannot be considered as generated or absorbed at a point source, but rather over almost the entire cell. Furthermore, the cell is heterogeneous and anisotropic; and, in cycling, the composition of the cell changes with time.

The discharge potential for a sintered-plate, nonwoven nylon separator-type spacecraft cell will average approximately 1.25 volts per cell for up to C/2 discharge rates. The charging potential for sealed NiCd cells can be between 1.35 and 1.50 volts per cell for moderate charging rates (up to C/5), depending upon the ambient temperature, the cell's previous history, and other parameters. The tendency for the cell to form hydrogen gas at the negative electrode (Cd) and oxygen at the positive electrode (Ni) during charge is modified or accounted for by several design features. Generally, the hydrogen gas is not formed at the negative electrode until the cadmium is almost fully charged. The evolution of hydrogen during charge is thereby delayed by having a positive limited cell in which there is 1.3 to twice as much negative capacity as there is positive plate capacity; i.e., under normal cycling, the Cd plate is never fully charged. However, the evolution of oxygen at the nickel plate is not so much prevented as accounted for. The oxygen gas will recombine with the charged cadmium at the negative plate, and, in the reaction, the cadmium is discharged (Cd(OH)_2). This recombination is aided by the high plate porosity (providing more activation sites) and by a thin, nonwoven, porous nylon separator with a minimum amount of electrolyte, providing a shorter and easier path for the oxygen to get from the positive to the negative plate. This recombination of oxygen can be accelerated by allowing the cell to stand or to discharge.

For reverse charging, (forced discharge in excess of a cell's capacity), the nickel plate, having less capacity, is the first to be discharged completely and would liberate hydrogen if some manufacturers did not add a small amount of cadmium in the nickel plate. The nickel plate then has its cadmium charged before it liberates hydrogen. This design feature allows a cell to be reverse-charged slightly, as can happen when three or more cells are cycled in series, without the liberation of hydrogen. Table 1 provides the physical characteristics of the nickel-cadmium electrodes.

Table 1
Nickel-Cadmium Electrode Characteristics.

Parameter	Nickel plate (sintered)	Cadmium plate (sintered)
No. of plates per cell	10	11
Length (cm)	7.05	6.95
Width (cm)	7.0	7.10
Thickness (cm)	0.092	0.076
Dry weight (gm)	144 (10 plates)	162 (11 plates)

PROCEDURE

The alumel-chromel thermocouples (Aero-Pak, Catalog number T-77M-8MK8B) that were used had a 10-mil outside diameter and were constructed as a two-element, concentric cable with a powdered insulator inside and an Inconel coating outside. The Inconel coating provided protection against the 30 percent KOH electrolyte. Teflon tubing was flattened into an oval shape by hydraulic press and threaded around the thermocouples to prevent them from shorting out the cell plates. The protected thermocouples were then placed into channels cut into the plate, with the top of the tubing (Figure 1) flush with the plate surface.

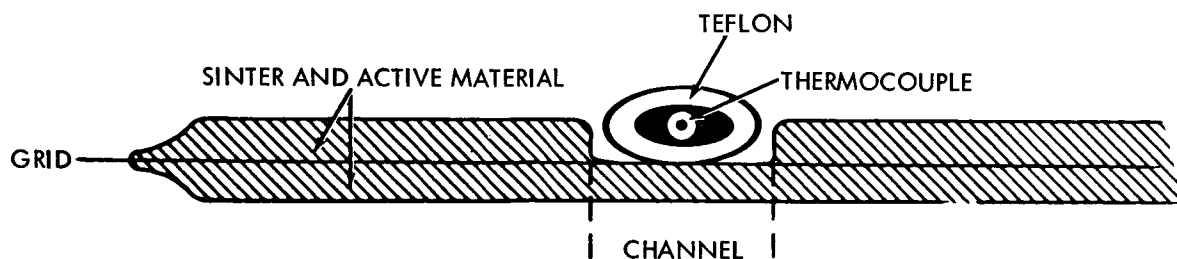


Figure 1 - Cross-sectional View of Thermocouple Placed in Plate Channel.

The channels in the plates were produced by milling away the active material and the sinter down to the plate grid. The thermocouples were then positioned as shown, and the cells assembled using a 10-mil, nonwoven nylon separator. The plate stack then was placed in a plastic case with the thermocouples protruding through the case top and fastened in a suitable mounting (Figure 2). To retard leakage, the assembly was then potted in a thin layer of epoxy.

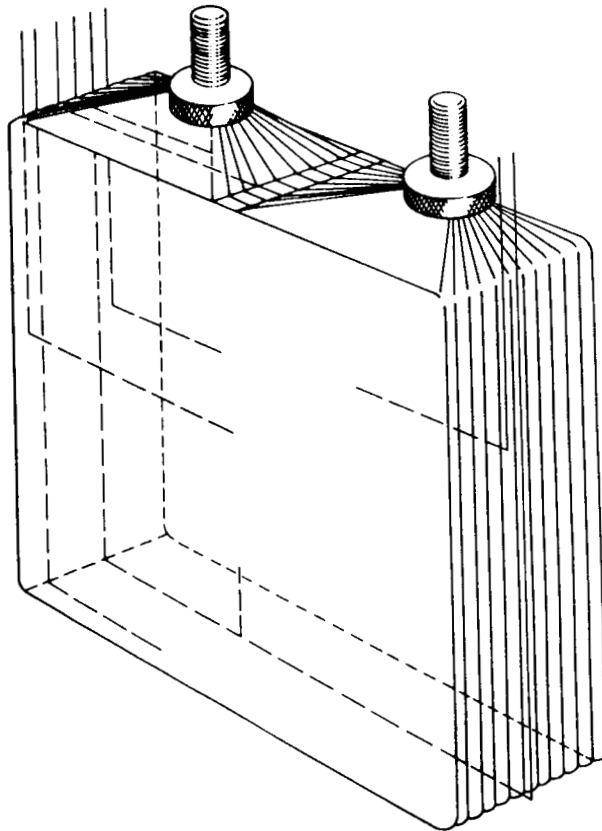


Figure 2 - Thermocouples in NiCd Plate Stack.

The thermocouples were connected to an ice bath. The resulting thermocouple voltages, the current shunt voltage, and cell voltages were connected to a multipoint recorder. The cell was automatically charged to a fixed voltage and discharged across a predetermined resistance during a 90-minute orbit.

RESULTS

The ambient temperature for these tests was 24°C. Figure 3 shows the results of the cell being charged at a 5.3-amp rate to a voltage limit of 1.49 volts. The cell is initially cool, and, for the endothermic reaction of charging, cools further. The cooling continues until the cell is approximately 60 percent charged. The cell

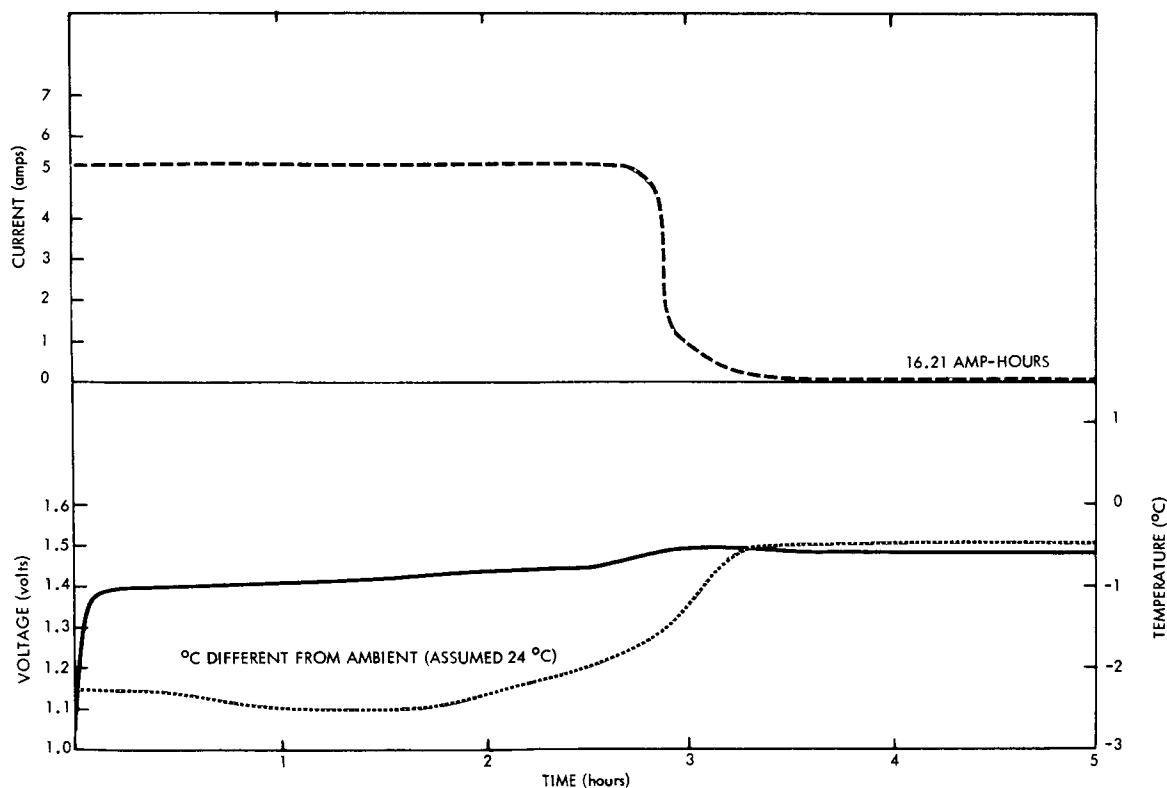


Figure 3 - Graph Showing Voltage Limit Charge.

reaction for the end of charge is less efficient than the initial charging, and the cell begins to heat. This temperature rise continues until the voltage rises (possibly a gassing potential), and the power supply abruptly reduces the charging current after 16.21 ampere-hours (a cell's rated capacity is generally less than its actual capacity).

The 5-amp constant-current discharge continues for 13.3 ampere-hours before the cell passes through zero terminal voltage (Figure 4). The cell's internal temperature was initially 2C° above ambient and increased to 6C° above ambient temperature to the point where the positive nickel plates were depleted and the voltage decreased sharply through zero to a negative voltage. The cadmium plates, having more

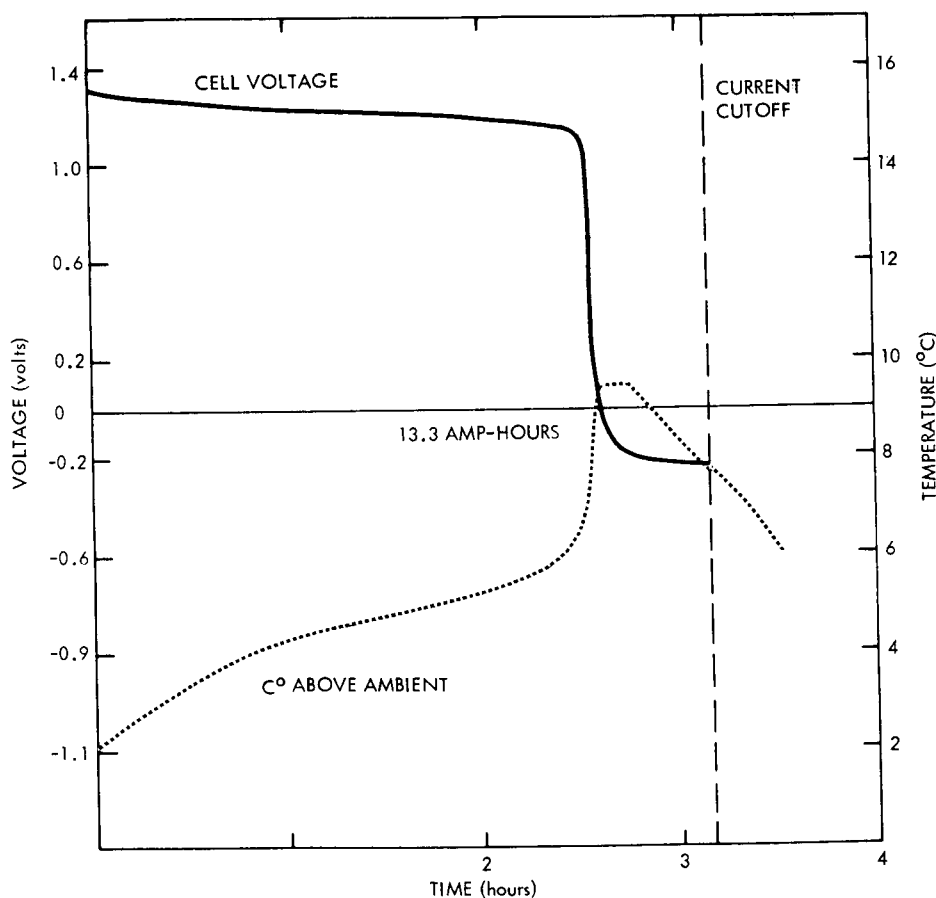


Figure 4 - Graph Showing 5-Ampere Constant Current Discharge.

capacity, were still being discharged. The temperature maximum or "hump" always occurred when the cell was fully discharged. This phenomenon was possibly caused by either cell polarization or some other transition state and not by gassing, as will be shown in the next graph.

The discharge across a fixed resistance (Figure 5) shows cell voltage decreasing as capacity decreases; thus the discharge current decreases. This graph differs from the previous one in that the current was not constant and in that the voltage passed through a second level (generally called the graphite step). After the voltage and current have decreased to 20 percent of their former values, the cell internal temperature passes through a maximum of almost 10°C above ambient. A pressure gage attached to the cell indicated a decrease in pressure (a common effect for the discharge of a NiCd cell). Thus the sudden temperature rise was not caused by gassing.

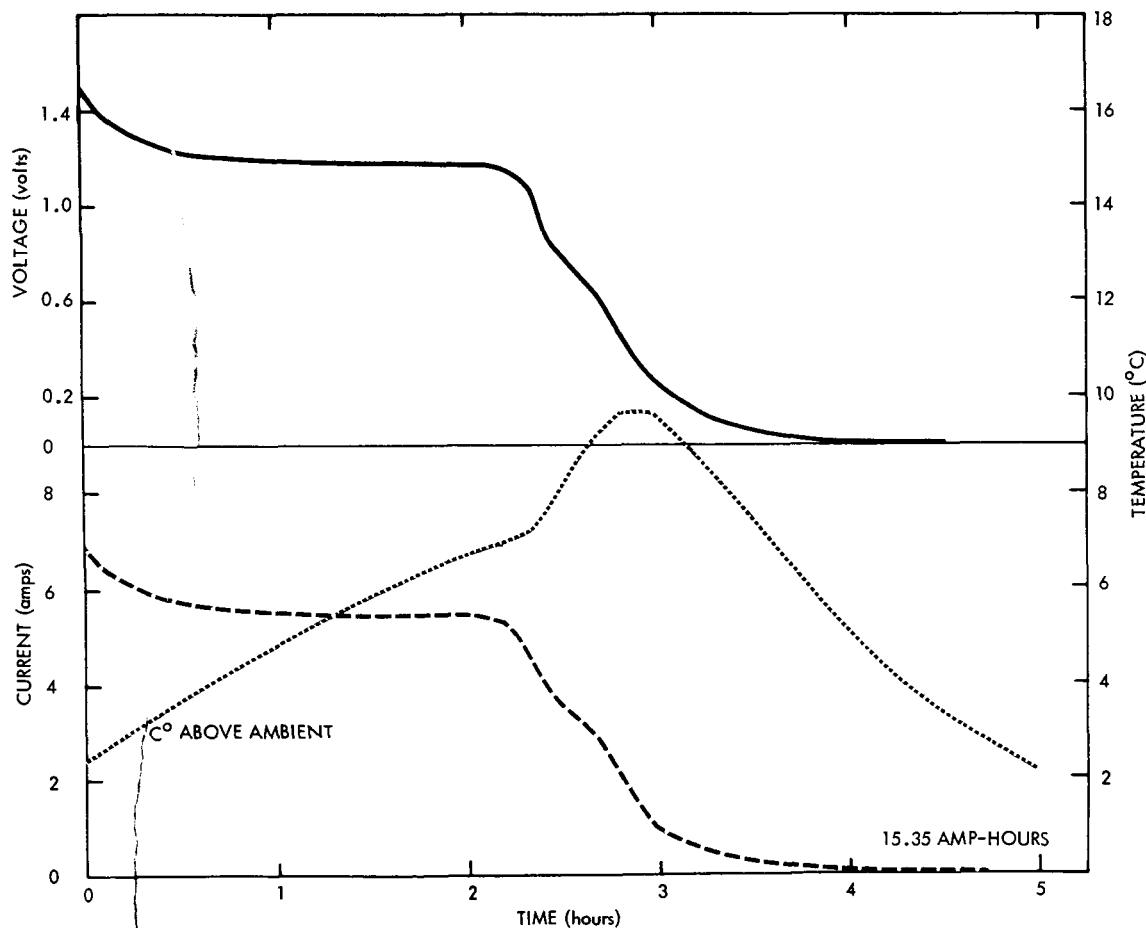


Figure 5 - Graph Showing Discharge Across a Fixed Resistance.

The typical cycle of a 12-ampere-hour NiCd cell (Figure 6) occurs during a 90-minute orbit consisting of a 60-minute charge to a voltage limit (1.49v) and a 30-minute discharge across a resistive load (approximately a 37 percent depth of discharge orbit). The internal temperature cycles 3°C about the ambient temperature.

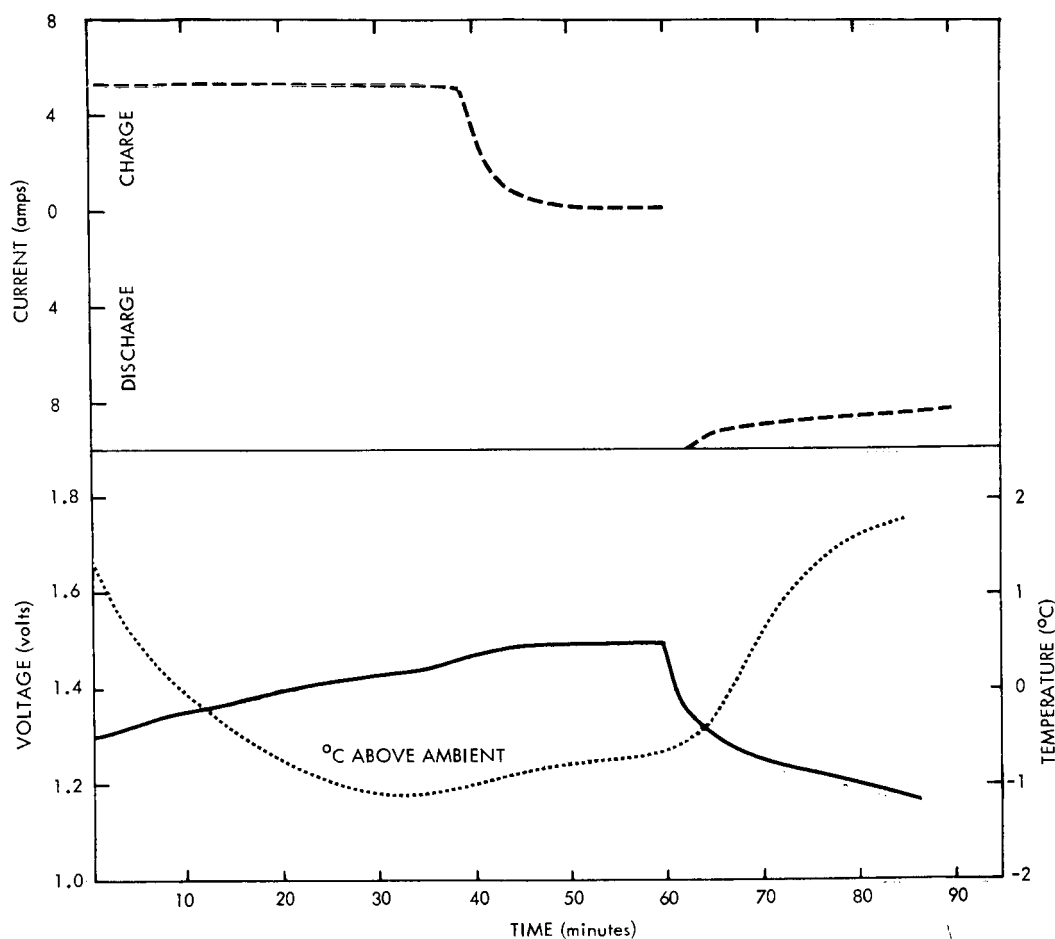


Figure 6 - Typical Cycle of 12 Ampere-hour NiCd Cell.

The discharge of a cell through a power supply (to maintain a constant current) in excess of the cell's capacity produces a negative cell voltage, gassing, and is known as reverse charging. Figure 7 shows the temperature and voltage curves of a 12-ampere-hour thermocouple cell that had a 5-amp current forced through it in a discharge direction for 6 hours (30 ampere-hours). At point A, the cell has just

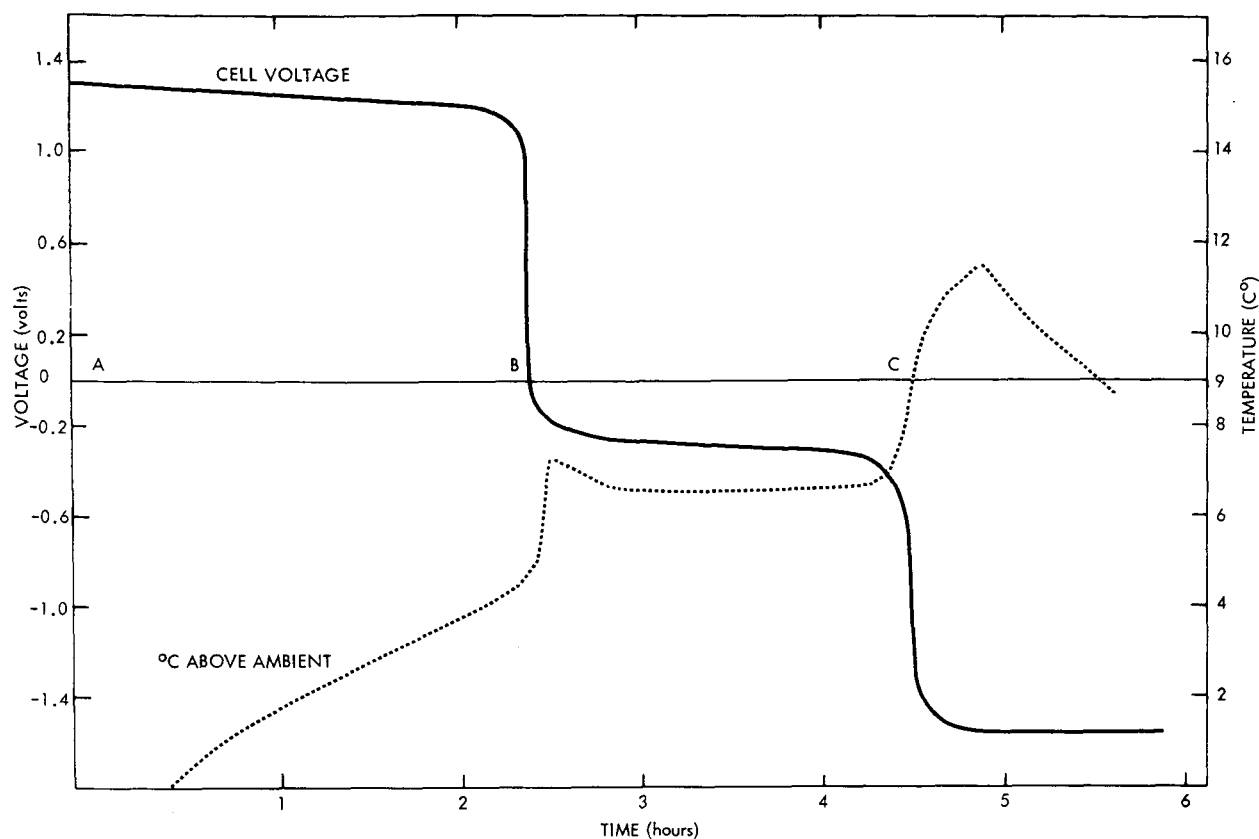


Figure 7 - Graph Showing 5-Ampere Constant Current Discharge and Reverse Charge.

completed a full charge and is cool. As the cell is discharged (between points A and B), the voltage drops slowly, and cell temperature rises. Approaching point B, the positive (Ni) plates of the cell are completely discharged; thus the cell is depleted of capacity, and the voltage drops suddenly toward zero. However, since the cell continues to be once-discharged at 5-amperes, the voltage passes zero and becomes negative (-0.15 to -0.3v). If the cell is open-circuited at this point, the cell voltage will recover to a positive value with the potential of the nickel plates being about 0.9 volt above the potential of the cadmium plates (which is less than the normal open-circuit voltage of a discharged cell). The internal temperature has gone

through a maximum, and, since the IV power has decreased, this suggests some sort of a transition state of the plates. Between points B and C, the voltage and temperature are roughly constant, and the cell gasses violently. The gas was determined to be H_2 on a gas chromatograph. At point C after approximately 24 ampere-hours (200 percent), the cadmium plates are depleted and the cell voltage drops to -1.56 volts. Again the temperature increase to a maximum suggests another transition state. The cell is now gassing H_2 and O_2 and will maintain its negative voltage, while on stand, for at least 3 days.